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(19) (CA) **CANADIAN PATENT** (12)

(54) Cleaning Compositions

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Abstract

Aqueous hypochlorite bleach compositions are provided comprising from 0.1% to 5.0% of a C_{10}-C_8 alkyl C_1-C_4 alkyl diamine oxide or a C_8-C_{18} alkyl substituted betaine together with from 0.001% to 0.25% of an organosilican quaternary ammonium compound containing a C_{16}-C_{20} alkyl group, the compositions having a viscosity of $\geq$ 200 centipoises at 20°C and an ionic strength of less than 5.0 g moles/dm^3.

Field of the Invention

This invention relates to hypochlorite bleach compositions and in particular to aqueous hydrochlorite bleaches containing a bactericidal material.

Background of the Invention

Aqueous bleach compositions containing alkali metal hypohalites, particularly sodium hypochlorite, have been known for many years. Because of their powerful oxidising action they have also been acknowledged to be powerful germicides and have been used extensively where this property is beneficial, e.g. in the cleaning of baths, wash basins, flush toilets, drains and ceramic tile floors. However, it has long been recognised that the germicidal effectiveness of surface treatments using such materials is limited by the relatively short period of time during which the aqueous composition containing the hypohalite is in contact with the surface concerned. Recent developments in the formulation of hypochlorite bleach products have shown a trend towards the use of higher viscosities, viz. 100 centistokes or greater, and this will increase the retention of such products on non horizontal surfaces.

Nevertheless, the increase in retention time introduced by such a thickened formulation will not be particularly significant, being measured in seconds or at most minutes, and a need exists for a bactericidal and germicidal material that is capable of retention on a target surface for much longer periods.

Quaternary ammonium compounds, in general, are known to have bactericidal characteristics, and certain water soluble quaternary ammonium surfactants such as cetyl pyridinium bromide are very effective antibacterial agents. Polymeric dialkyl siloxane and silane structures are well known as having a high affinity for siliceous surfaces and thus a combination of a quaternary ammonium function and a siloxane or silane grouping might be expected to provide a long lasting antibacterial effect on siliceous surfaces of the type mentioned above. Such is indeed the case and the antimicrobial effectiveness of a representative alkoxy silane (3(trimethoxy silyl)propyl dimethyl octadecyl ammonium chloride) on a variety of surfaces, siliceous, metallic, synthetic, plastic and natural textile in nature, has been reported by A.J. Isquith et al in J. Applied Microbiology, 24 (6), 1972, pp. 859-863.

However, the incorporation of quaternised alkoxy silanes into aqueous cleaning or bleaching compositions poses considerable difficulty. All alkoxy silanes of this type will hydrolyse in contact with water, to produce the corresponding silanol derivative which themselves are prone to polymerisation via condensation of the silanol groups. The polymerised materials are less surface substantive than the parent silanols.

In the case of the more water soluble alkoxy silanes, containing a C_{12}-C_{14} alkyl group in the quaternary ammonium portion of the molecule; the materials display physical stability in aqueous alkalis and commercial aqueous hypochlorite and also display surface substantive properties. However, in the presence of hypochlorite-stable surfactants, surface substantivity is markedly impaired due to solubilisation into surfactant micelles. Furthermore, these shorter chain alkyl quaternised alkoxy silanes do not display broad range antibacterial efficacy.

Quaternary alkoxy silanes containing an alkyl chain longer than C_{14} are less water soluble and do not even display long term stability in aqueous alkaline solutions but precipitate therefrom, probably in polymerised, and hence antibacterially ineffective, form.

However, it has surprisingly been found that those quaternised alkoxy silanes containing a C_{16}-C_{20} alkyl group can be incorporated into an aqueous hypochlorite bleach composition to produce a physically stable product capable of delivering a long lasting antibacterial effect to siliceous surfaces treated therewith.

Aqueous hypochlorite bleach compositions forming suitable vehicles for the delivery of the quaternised alkoxy silanes should be free of anionic surfactants and preferably should have a low ionic strength.

Accordingly the present invention provides an aqueous bleaching composition comprising from 0.1%-5% by weight of a surfactant selected from amine oxides of formula $R_4R_5R_6N^{+}O$, wherein R_4 is a C_{10}-C_{18} alkyl group and R_5 and R_6 are C_1-C_4 alkyl groups substituted betaines of formula $R_7R_8R_9N^{+}$-$R^{10}COO^{-}$ wherein R_7 is a C_8-C_{18} alkyl group, R_8 and R_9 are C_1-C_4 alkyl groups and R_{10} is a C_1-C_4 alkylene group, and mixtures thereof, from 1.0% to 12.0% by weight of an alkali metal hypochlorite and from 1.0% to 15% by weight of inorganic compounds other than hypochlorite, said composition having a pH in the range from 10 to 12, wherein the composition also contains from 0.001-0.25% by weight of an organosilicon quaternary ammonium compound of formula

$$(R_3)_y(R_3O)_{3-y}Si(CH_2)_3\overset{R_2}{\underset{R_2}{N^{+}}} - R_1\ X^{-}$$

wherein R_1 is C_{16}-C_{20} alkyl, R_2 is C_1-C_4 alkyl, R_3 is C_1-C_4 alkyl, y is an integer from 0 to 2, and X^{-} is a water soluble anion or the silanol derivative thereof wherein R_3 is H;

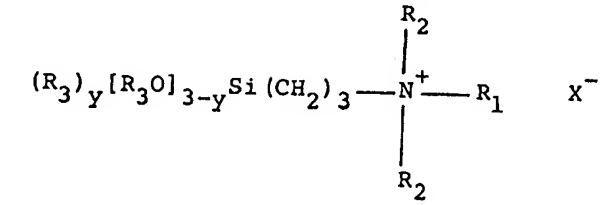
wherein the ionic strength of the composition is less than 5.0g moles/dm^3 and wherein the composition is free of anionic surfactant species.

Preferably the composition contains from 0.005% to 0.05% and most preferably from 0.01% to 0.03% of the organosilicon quaternary ammonium compound. Preferably R_1 is a C_{18} alkyl group.

In highly preferred compositions in accordance with the invention, the viscosity of the composition is at least 200 centipoises at 20°C and comprises alkali metal hypochlorite in an amount of from 8% to 10% by weight, a C_{14}-C_{15} alkyl dimethyl amine oxide as the only surfactant in an amount of from 1.0 to 1.5% by weight together with at least 400 ppm of a monocyclic or bicyclic monoterpene alcohol or the ester thereof with a C_2-C_3 alkanoic acid, and the composition has an ionic strength of less than 4.0 g moles/dm^3.

The above mentioned reference to viscosity is to the dynamic viscosity η which is measured by a Brookfield RVT viscometer and for the purposes of this specification measurements are made with Spindle No. 3 at 100 rpm and a liquid temperature of 20°C. Fluid viscosity can also be expressed as the kinematic viscosity γ in centistokes as measured by an Ostwald viscometer and is characterised by the expression $\gamma = \eta/\rho$ where η is the dynamic viscosity in centipoises and ρ is the density in g/cm^3. Compositions in accordance with the present invention have a density in the range from 1.10 to 1.25 g/cm^3, typically approximately 1.15 g/cm^3, so that the numerical value of the kinematic viscosity in centistokes is slightly less than that of the dynamic viscosity in centipoises.

Organosilicon quaternary ammonium compounds having the desired combination of broad spectrum antibacterial activity and physico chemical stability in compositions in accordance with the invention have the general structure:



wherein R_1 is C_{16}-C_{20} alkyl, R_2 is C_1-C_4 alkyl, R_3 is C_1-C_4 alkyl, y is an integer from 0 to 2, and X^-

is a water soluble anion. A preferred chain length for R_1 is C_{18} for antibacterial efficacy reasons, and for reasons of cost and ease of preparation R_2 and R_3 are usually methyl. In aqueous alkaline solution the (R_3O) groups will hydrolyse to give the silanol derivative so that references herein to the organic silicon quaternary ammonium compound include the silanol derivative thereof. X^- is normally halide, particularly chloride, but can also include methosulphate, acetate or phosphate.

The level of incorporation of the organosilicon compound is from 0.001% to 0.25% based on the total weight of the composition but is more usually in the range of from 0.005% to 0.05% and most preferably from 0.01% to 0.03% by weight.

In compositions in accordance with the invention, the hypochlorite bleach, and the alkali metal chloride and chlorate salts which accompany it in commercially available material, provide the majority and preferably substantially all of the ionic strength requirement. This will normally result in an ionic strength of at least 3.0 g moles/dm^3. Ionic strength values in excess of 5.0 g moles/dm^3 are not desirable because of their adverse influence on the stability of both the hypochlorite and organosilicon quaternary ammonium compound components. Preferably the ionic strength is less than 4.0 g moles/dm^3 and values in the region of 3.4-3.8 g moles/dm^3 are considered to be optimum where a stable product of viscosity $\leq$200 centipoises is desired.

The alkali metal hypochlorite may be a lithium, potassium or sodium hypochlorite and the level of hypochlorite in the composition is normally arranged to lie in the range 1-12%, preferably 5-10% by weight. Customarily hypochlorite bleach compositions contain approximately 6% or 9% hypochlorite by weight. However, the activity of chlorine bleaching compositions is conventionally expressed in terms of the weight percentage of available chlorine in the composition, and the actual weight percentage of bleaching species is arranged to provide the desired level of 'available chloride'. The preferred hypochlorite species is sodium hypochlorite which contains 95.3% available chlorine.

Alkali metal hypochlorites are commercially available as aqueous solutions containing 10-15% by weight 'available chlorine' and the bulk suppliers normally produce material having available chlorine contents towards the upper end of this range viz. 12-14% by weight. These commercially available hypochlorite solutions contain other salts as byproducts or contaminants, more specifically free alkalinity in the form of alkali metal hydroxide and alkali metal carbonate, and alkali metal chloride. Low levels of other species such as sodium chlorate are also believed to be formed during hypochlorite manufacture but their chemical stability is sufficiently low that they have largely decomposed by the time the hypochlorite is employed in product formulations. The levels of the byproduct materials depend on the processing conditions employed in the manufacture of the hypochlorite but in general they fall within the ranges

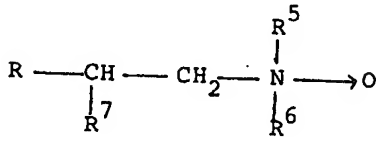
0.2 - 1.0% alkali metal hydroxide
0.01 - 0.1% alkali metal carbonate
10.0 - 18.0% alkali metal chloride

expressed as a weight percentage of the hypochlorite solution as supplied.

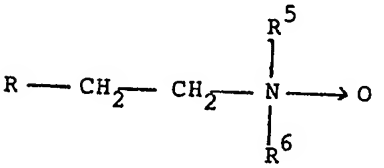
Amine oxides useful in the present invention have the formula $R_4R_5R_6N \rightarrow O$ wherein R_4 is a C_{10}-C_{18} alkyl group and R_5 and R_6 are C_1-C_4 alkyl groups. The amine oxide is present in an amount of from 0.5% to 5%, more preferably from 0.5% to 2.5% and, in preferred embodiments of the invention in which the R_4 average chain length 14 carbon atoms, from 1% to 1.5% by weight of the composition. The R_4 group may be linear or branched and may be derived from natural or synthetic hydrocarbon sources. For the purposes of the present invention linear groups are defined as including moieties incorporating up to 25% methyl branching, predominantly in the 2-position relative to the nitrogen atom of the amine oxide.

Methyl branching on the alkyl chain also predominates in those amine oxides useful in the present invention in which the R_4 group is branched, rather than linear in nature.

Commercially available sources of these amine oxides are normally a mixture of



where R_7 is methyl and



which mixture arises as a result of the processing route used to form the precursor alcohol or aldehyde. This route involves carbonylating or hydroformylating an olefin, preferably a linear -olefin and leads to a mixture of the desired branched chain aldehyde or alcohol of the same carbon number. For olefin starting materials having a range of carbon chain length, the resultant alcohol or aldehyde mixture contains compounds of different carbon number and isomers containing straight chain and 2-alkyl branched chain alkyl groups. A typical commercially available mixture comprises 65 to 75% by weight C_{13} and 35 to 25% by weight C_{15} amine oxides with approximately 50% by weight straight chain and 50% by weight 2-alkyl branched chain where the 2-alkyl group is predominantly methyl. These are available from ICI under the trade mark Synprolam 35 DMO as a 30% aqueous solution. The branched chain amine oxides and mixtures thereof with linear chain amine oxides are used at levels towards the upper end of the range viz. $\geq$2% by weight of the composition and typically from 2.0% to 2.5% by weight.

Although the above-described mixture of straight chain and branched chain alkyl dimethyl amine oxides has been found suitable for the purposes of the invention, their use does not constitute the most preferred execution of the invention. This is because a bleaching composition containing 8-10% hypochlorite and an amine oxide in which the long chain alkyl group has a carbon number of about 63.3 requires an ionic strength of at least 4.7 g moles/dm^3

to achieve the preferred product viscosity of at least 200 cp. This level of ionic strength is believed to make the storage stability of the hypochlorite bleach less than that which is considered desirable for the expected shelf life of the product. The preferred amine oxide structure for 'thickened' products having a viscosity of $\geq$200 cp is one in which R_4 has an average chain length in the range C_{14}-C_{15}. Compositions containing these preferred amine oxides require a lower amine oxide level viz. <2.0%, more typically 1.0-1.5% and also a lower ionic strength viz. 3.0 g moles/dm^3 minimum in order to achieve target viscosity. Another hypochlorite-stable surfactant suitable for the purposes of the present invention is a substituted betaine of formula

$$R_7R_8R_9N^+-R_{10}COO^-$$

wherein R_7 is a C_8-C_{18} alkyl group, preferably a C_{10}-C_{14} alkyl group, R_8 and R_9 are C_1-C_4 alkyl groups, more preferably methyl groups, and R_{10} is a C_1-C_4 alkylene group more preferably a C_2-C_3 alkylene group. Specific examples include octyl, decyl, dodecyl, tetradecyl and hexdecyl betaines in which R_{10} is an ethylene or propylene group and R_8 and R_9 are methyl groups. Both of these reductions in ingredient level lead to improved storage stability and also lower the cost of the product.

A highly preferred optional component for hypochlorite bleach compositions suitable for incorporating the quaternised alkoxy silanes, particularly those utilising an amine oxide wherein R_1 has an average chain length of about 14 carbon atoms, is at least one monocyclic or bicyclic monoterpene alcohol or the ester thereof with a C_2-C_3 alkanoic acid, in an amount of at least 400 ppm based on the weight of the composition.

Monocyclic and bicyclic monoterpene alcohols and their esters with C_2-C_3 alkanoic acids are known and used as ingredients in fragrances, including those employed in detergent compositions. As such their level of incorporation varies from 10 - 500 ppm of the composition depending on the perfume formulation and the nature of the detergent composition.

It has now surprisingly been found that in aqueous hypochlorite bleach solutions containing from 1.0% to 2.5% of a C_{14}-C_{16} amine oxide as the only surfactant, the incorporation of at least 400 ppm of at least one monocyclic or bicyclic monoterpene alcohol or the ester thereof with C_2-C_3 alkanoic acid provides an enhancement of the viscosity of the bleach solution and facilitates the generation of viscosities of 200 centipoises and greater at 20°C. Preferably the monoterpene alcohol or ester is present in an amount of at least 600 ppm. Examples of materials demonstrating this effect are isoborneol, isobornyl acetate, dihydroterpineol and dihydroterpinyl acetate.

The mode of operation of these materials in this system is not fully understood but it is hypothesised that in the absence of anionic surfactants hydrogen bonding occurs between adjacent alcohol functions of the relatively water insoluble terpene alcohols held in the amine oxide micelles. This leads to the formation of an extended micellar structure in the solution which provides an increased viscosity.

Thickened aqueous hypochlorite bleach compositions including the above mentioned terpene alcohol derivatives are particularly preferred for the incorporation of the quaternised alkoxy silane antibacterial component as such compositions utilise the minimum amounts of amine oxide surfactant and ionic salts necessary to generate the desired product viscosity and hence enhance the stability of the quaternised alkoxy silanes.

As stated hereinbefore, the salts accompanying the hypochlorite bleach provide most if not all of the ionisable species necessary for the ionic strength requirement. However, other non surface active organic or inorganic compounds can be added where necessary to provide an ionic strength in the desired range.

The ionisable compound(s) can be inorganic in nature e.g. hydroxide, sulphate, halide, (particularly chloride), carbonate, nitrate, or orthophosphate, pyrophosphate, or polyphosphate, or organic such as formate, acetate or succinate.

In the preferred embodiments of the invention inorganic compounds such as silicates and organic compounds incorporating oxidisable groups are avoided because of their tendency to have adverse effects on physical and/or chemical stability of the compositions on storage. Certain organic sequestrants such as the amino poly (alkylene phosphonates) salts can, however, be incorporated in an oxidised form in which they are not susceptible to attack by the hypochlorite bleach. Such sequestrants are normally present in amounts of from 0.1% to 0.5% by weight of the composition.

The ionic strength of the composition is calculated by means of the expression

$$\text{Total Ionic Strength } I = \sum \frac{C_i z_i^2}{2}$$

where C_i is the molar concentration of the ionic species in g moles/dm^3

z_i is the valency of the species.

The function $C_i z_i^2$ is calculated for each of the ionic species in solution, these functions are summed and divided by two to give the composition ionic strength.

The ionisable alkali metal compound normally comprises a caustic alkali such as sodium or potassium hydroxide either alone or in admixture with alkali metal salts. For product safety reasons the amount of caustic alkali is normally limited to a value in the range of from 0.5% to 2%, more usually from 0.75% to 1.5% by weight of the composition.

A desirable optional component of compositions in accordance with the invention is a perfume which is present at a level of from 0.01% to 0.5% preferably from 0.05% to 0.25% by weight of the composition. In the preferred thickened bleach compositions incorporating a monocyclic or bicyclic monoterpene alcohol component this can conveniently be incorporated in the perfume mixture.

The compositions are made by conventional mixing techniques. Because of the relatively low aqueous solubility of the organo silicon compound which is normally supplied as a solution in methanol, a premix of the amine oxide, perfume, added caustic alkali and water is normally prepared and the organo silicon compound is then added with vigorous agitation.

This mixture is then added to the hypochlorite solution to make the final product. Other orders of addition can be used but unless the amine oxide is present in the solution to which the organo silicon compound solution is added, problems of incomplete solution or precipitation can arise.

The invention is illustrated in the following examples in which percentages are expressed by weight of the composition unless otherwise stated.

In the Examples, reference to ingredients have been abbreviated as follows:

C_{15}DMAO	C_{15} alkyl dimethyl amine oxide in which the alkyl group is 95% C_{15} and approximately 50% of the alkyl groups contain methyl branching on the 2-carbon atom.
C_{14}DMAO	C_{14} alkyl dimethyl amine oxide in which the alkyl group is a predominantly linear C_{14} (94%) moiety. Available from Albright & Wilson Ltd. as Empigen OH.
NaCl	Sodium chloride
NaOH	Sodium hydroxide
NaOCl	Sodium hypochlorite
NaPyro	Tetra sodium pyrophosphate
K Pyro	Tetra potassium pyrophosphate

EXAMPLE 1

420 g of a 30% solution of C_{14} alkyl dimethyl amine oxide was added to 3555.6 g of demineralised water and 12.5 g of a perfume material containing 6.4 g of isobornyl acetate was dispersed therein. To this solution was slowly added, with vigorous agitation, 11.9 g of a 42% solution in methanol of 3(trimethoxy silyl) propyl dimethyl octadecyl ammonium

chloride (available from Dow Corning Ltd as DC 5700) to form a premix solution. 125 g of solid sodium hydroxide was dissolved in 5875 g of sodium hypochlorite solution (15.3% $AvCl_2$ solution supplied by ICI Ltd) and 4000 g of the premix was then blended with high shear agitation into this solution.

This composition had the following analysis, in percent by weight and had a density of 1.15 g/cm^2.

NaOCl	9.43 (= ~~9.9%~~ 9.0% available chlorine)	1.46 g moles/dm^3
NaCl	9.40	1.84 " " "
NaOH	1.25	0.36 " " "
Amine Oxide	1.26	
DC5700	0.05	
Perfume	0.125	
Water & Misc	78.485	
	100.000	

This product was a single phase solution having a dynamic viscosity of 270 centipoises as measured at 20°C with a Brookfield viscometer using the No. 3 spindle at 100 rpm on product that was 24 hours old.

The ionic strength of this composition was calculated to be 3.66.

EXAMPLE 2

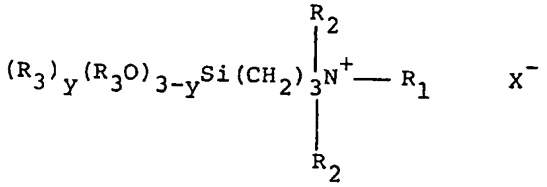
The following compositions are prepared according to the technique of Example 1:

	(a)	(b)	(c)	(d)
C_{14}DMAO		1.2	1.5	1.75
C_{15}DMAO	1.2			
DC5700	0.02	0.02	0.02	0.02
NaOH	1.0	1.0	1.0	1.0
NaOCl	9.0	9.0	9.0	9.0
NaCl	9.0	9.0	9.0	9.0
Isoborneol	0.05		0.06	0.04
Dihydroterpinyl acetate		0.06		
Water & Misc.	——— to 100 ———			
Viscosity (cp)	350	190	245	324

The density of each of these compositions is 1.15 g/ml and the ionic strength for each composition is calculated to be 3.5 g moles/dm^3. The product viscosity was measured at 20°C using the technique of Example 1.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A stable, aqueous bleaching composition consisting essentially of from about 0.1% to about 5% by weight of a surfactant selected from the group consisting of amine oxides of formula $R_4R_5R_6N\rightarrow O$, wherein R_4 is a C_{10}-C_{18} alkyl group and R_5 and R_6 are C_1-C_4 alkyl groups, substituted betaines of formula $R_7R_8R_9N^+$-$R_{10}COO^-$ wherein R_7 is a C_8-C_{18} alkyl group and R_8, and R_9 are C_1-C_4 alkyl groups, and R_{10} is a C_1-C_4 alkylene group; and mixtures thereof, from about 1.0% to about 12.0% by weight of an alkali metal hypochlorite and from about 1.0% to about 15% by weight of inorganic compounds other than hypochlorite, said composition having a pH in the range from about 10 to about 12, wherein the composition also contains from about 0.001 to about 0.25% by weight of an organosilicon quaternary ammonium compound of the formula



wherein R_1 is C_{16}-C_{20} alkyl, R_2 is C_1-C_4 alkyl, R_3 is C_1-C_4 alkyl, y is an integer from 0 to 2 and X^- is a water soluble anion; or the silanol derivative thereof wherein R_3 is H; wherein the ionic strength of the composition is at least about 3 g moles/dm^3 to less than about 5.0 g moles/dm^3, and wherein the composition is substantially free of anionic surfactant species.

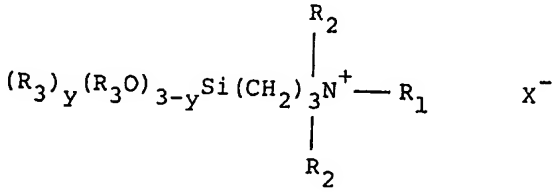
2. A bleaching composition according to claim 1 wherein R_1 is C_{18} and X^- is a halide anion.

3. A bleaching composition according to either one of claims 1 and 2 wherein the ionic strength of the composition is less than 4.0 g moles/dm^3.

4. A bleaching composition according to claim 1 wherein

an alkyl dimethyl amine oxide in which the alkyl group has an average carbon chain length of from 14 to 15 carbon atoms is the only surfactant species present.

5. A stable, aqueous bleaching composition consisting essentially of from about 1.0% to about 2% by weight of an amine oxide of formula $R_4R_5R_6N\rightarrow O$, wherein R_4 is an alkyl group having an average carbon chain length of 14 to 15 carbon atoms and R_5 and R_6 are methyl groups, from about 5.0% to about 10.0% by weight of an alkali metal hypochlorite and from about 1.0% to about 15% by weight of inorganic compounds other than hypochlorite, said composition having a pH in the range from about 10 to about 12, wherein the composition also contains from about 0.005 to about 0.05% by weight of an organosilicon quaternary ammonium compound of formula



wherein R_1 is C_{18} alkyl, R_2 is methyl, R_3 is methyl, y is an integer from 0 to 2 and X^- is a water soluble anion; or the silanol derivative thereof wherein R_3 is H; wherein the ionic strength of the composition is at least 3 g moles/dm^3 to less than about 4.0 g moles/dm^3, and wherein the composition is free of anionic surfactant species.

6. A thickened bleach composition according to claim 5 wherein the composition contains a monocyclic or bicyclic monoterpene alcohol or an ester thereof with a C_2-C_3 alkanoic acid in an amount of at least 400 ppm, whereby the composition has a viscosity of $\geq$200 centipoise at 20°C.

7. A thickened bleach composition according to claim 6 wherein the amine oxide level is from about 1.0% to about 1.5% and the monocyclic or bicyclic monoterpene alcohol or an ester thereof with a C_2-C_3 alkanoic acid is present

in an amount of at least about 600 ppm.

8. A thickened bleach composition according to claim 7 wherein the monocyclic or bicyclic monoterpene alcohol or an ester thereof with a C_2-C_3 alkanoic acid is selected from the group consisting of isoborneol, isobornyl acetate, dihydroterpineol, dihydroterpinyl acetate, and mixtures thereof.

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